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For: Method of Processing Surface of Nitride Semiconductor Crystal and Nitride Semiconductor Crystal Obtained with the Method

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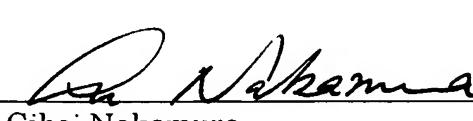
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## DESCRIPTION

### Method of Processing Surface of Nitride Semiconductor Crystal and Nitride Semiconductor Crystal Obtained with the Method

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#### Technical Field

The present invention relates to a method of processing a surface of a nitride semiconductor crystal and a nitride semiconductor crystal obtained with the method. More specifically, the present invention relates to a method of processing a surface of a nitride semiconductor crystal with a decreased depth of a surface scratch or a decreased thickness of a damaged layer, and a nitride semiconductor crystal obtained with the method.

#### Background Art

15. Attention has been focused on a micromachining technique for a semiconductor crystal while higher integration of semiconductor devices has been performed. A technique for processing a semiconductor crystal to obtain a flat surface thereof (a planarization technique) is important as a basis of the micromachining technique for a semiconductor crystal.

20. In these days, a CMP (chemical mechanical polishing) method, that is, chemical and mechanical polishing using abrasive slurry consisting of an abrasive solution and abrasive grains is mainly used as a method for processing a semiconductor crystal to obtain a flat surface.

25. Though chemical surface processing is possible for a silicon crystal or the like which is chemically active (for example, it is soluble in hydrofluoric acid), a nitride semiconductor crystal such as a group III nitride semiconductor crystal is chemically inert (stable) and has a dependence on mechanical processing. The "mechanical processing" mentioned here means surface processing of a crystal in which abrasive

grains are interposed between the crystal and a turn table (hereafter referred to as a "surface plate") and the surface plate is moved relative to the crystal to cut or polish a crystal surface with friction between the abrasive grains and the crystal surface.

During the mechanical processing, deep scratches are generated on the crystal  
5 surface with the abrasive grains, and a thick layer of a disordered crystal (hereafter referred to as a "damaged layer") is formed due to the friction between the crystal surface and the abrasive grains (see Yamamoto, *KESSHOUKOUGAKU HANDBUKKU* (*Handbook of Crystal Engineering*), first edition, Kyoritsu Shuppan Co. Ltd., September 25, 1990, pp. 421-423). Since existence of the deep scratch on  
10 the crystal surface or the thick damaged layer disturbs micromachining and degrades semiconductor characteristics, the scratch on the crystal surface and the damaged layer must be removed with further etching or the like.

#### Disclosure of the Invention

15 An object of the present invention is to provide a method of processing a surface of a nitride semiconductor crystal with a decreased depth of a surface scratch or a decreased thickness of a damaged layer, and a nitride semiconductor crystal obtained with the method.

To attain the above-described object, a method of processing a surface of a  
20 nitride semiconductor crystal according to the present invention is characterized in that, a surface of a nitride semiconductor crystal is brought into contact with a liquid containing at least Na, Li or Ca as a processing solution. The processing solution may be a liquid containing at least Na, which can have an Na content of 5-95 mol%. In addition, the processing solution may be a liquid containing at least Li, which can have  
25 an Li content of 5-100 mol%. An  $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$  semiconductor crystal ( $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq x + y \leq 1$ ) or the like can be processed as the nitride semiconductor crystal.

In addition, a nitride semiconductor crystal according to the present invention is a nitride semiconductor crystal having a maximum depth of a surface scratch of at most

0.01  $\mu\text{m}$  or an average thickness of a damaged layer of at most 2  $\mu\text{m}$ , which is obtained with the above-described method of processing a surface of a nitride semiconductor crystal.

As described above, according to the present invention, a method of processing a surface of a nitride semiconductor crystal with a decreased depth of a surface scratch and a decreased thickness of a damaged layer as well as a nitride semiconductor crystal obtained with the method can be provided with a surface of a nitride semiconductor crystal being brought into contact with a liquid containing at least Na, Li or Ca as a processing solution.

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#### Brief Description of the Drawings

Fig. 1 is a view for describing a method of processing a surface of a nitride semiconductor crystal according to the present invention.

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Fig. 2 is a perspective cross-sectional view of a surface plate used in the present invention.

Fig. 3 is a perspective cross-sectional view of another surface plate used in the present invention.

#### Best Modes for Carrying Out the Invention

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Referring to Fig. 1, a method of processing a surface of a nitride semiconductor crystal according to the present invention is characterized in that, a surface of a nitride semiconductor crystal 11 is brought into contact with a liquid containing at least Na, Li or Ca as a processing solution 15. More specifically, by reference to Fig. 1, nitride semiconductor crystal 11 fixed on a crystal holder 12 is pressed against a surface plate 14 fixed on a rotation axis 13 with processing solution 15 interposed therebetween, and rotation axis 13 is rotated to move surface plate 14 relative to nitride semiconductor crystal 11 to process the surface of the nitride semiconductor crystal.

The surface plate used in the present invention is not specifically limited. As an

example, a surface plate A 24 as shown in Fig. 2, which has a flat surface for processing a crystal surface, or a surface plate B 34 as shown in Fig. 3, which has a surface having grooves formed thereon for processing a crystal surface, is preferably used. Though a depth D, a width W and a pitch P of the groove of the surface plate B are not specifically limited, depth D of 0.5-3 mm, width W of 0.5-3 mm, and pitch P of 1-5 mm are preferred.

The "liquid containing Na, Li or Ca" described here means a liquid containing Na or a Na compound such as Na, NaNH<sub>2</sub> or NaX (X indicates a halogen element such as I, Br or Cl, which is the same in the following), a liquid containing Li or a Li compound such as Li, LiNH<sub>2</sub> or LiX, or a liquid containing Ca or a Ca compound such as Ca or CaX<sub>2</sub>, which also includes a liquid containing two or more elements of Na, Li and Ca.

Nitrogen (N) in the nitride semiconductor crystal is dissolved into the liquid containing Na, Li or Ca, and thereby the surface of the nitride semiconductor crystal is etched. When a GaN crystal as one of the nitride semiconductor crystal is brought into contact with liquid Na, for example, a surface of the GaN crystal is etched with a reaction expressed as the following formula (1).



In the method of processing a surface of a nitride semiconductor crystal according to the present invention, the processing solution may be a liquid containing at least Na, which can have an Na content of 5-95 mol%. When Li or Ca is added to Na in the processing solution, an amount of dissolved nitride semiconductor crystal into the processing solution increases, and thus a processing speed increases.

When Li is added to Na, the Na content in the processing solution is preferably 5-60 mol%, and more preferably 10-50 mol% in terms of increasing the processing speed. When Ca is added to Na, the Na content in the processing solution is preferably 20-95 mol%, and more preferably 50-90 mol% in terms of increasing the processing speed.

In addition, in the method of processing a surface of a nitride semiconductor

crystal according to the present invention, the processing solution is preferably a liquid containing at least Li in terms of increasing the processing speed. A Li content in the processing solution is preferably 5-100 mol%, more preferably 30-100 mol%, and further preferably 50-100 mol%.

5        In addition, in the method of processing a surface of a nitride semiconductor crystal according to the present invention, a processing temperature is preferably at least a melting point and at most a boiling point of the processing solution, and more preferably at least a temperature 100 °C higher than the melting point and at most a temperature 100 °C lower than the boiling point of the processing solution. When a  
10      temperature of the processing solution is at least a temperature 100 °C higher than the melting point, an amount of nitrogen dissolved into the processing solution increases, and when the temperature is at most a temperature 100 °C lower than the boiling point, evaporation of the processing solution is decreased, which enables efficient utilization of the processing solution.

15      Table 1 shows melting points and boiling points of various liquids used as the processing solution, each containing Na, Li or Ca. The melting point and boiling point of the processing solution are determined according to composition of the processing solution, and then the processing temperature can be determined as appropriate according to the viewpoint as described above.

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Table 1

Processing Solution	Melting Point (°C)	Boiling Point (°C)
Na	97.7	892
Li	186	1609
Ca	850	1200
NaNH <sub>2</sub>	210	400
NaI	651	1300
NaBr	747	1390
NaCl	801	1413
LiNH <sub>2</sub>	374	430
LiI	446	1191
LiBr	500	1265
LiCl	605	1325-1360
LiF	848	1681
CaI <sub>2</sub>	740	1100
CaBr <sub>2</sub>	730	810
CaCl <sub>2</sub>	772	>1600

The method of processing a surface of a nitride semiconductor crystal according to the present invention can be preferably applied to processing of a surface of an Al<sub>x</sub>Ga<sub>y</sub>In<sub>1-x-y</sub>N semiconductor crystal ( $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq x + y \leq 1$ ). The method can be widely applied to the nitride semiconductor crystal having nitrogen as an element of the crystal, regardless of Al, Ga and In contents.

With the above-described method of processing a surface of a nitride semiconductor crystal, the nitride semiconductor crystal having a maximum depth of a surface scratch of at most 0.01 μm can be obtained. Since the method of processing described above only uses a chemical method rather than a physical method of cutting or polishing with abrasive grains, the surface scratch due to friction between the abrasive grains and the crystal surface is not generated.

In addition, with the above-described method of processing a surface of a nitride

semiconductor crystal, the nitride semiconductor crystal having an average thickness of a damaged layer of at most 2  $\mu\text{m}$  can be obtained. Since the method of processing described above only uses a chemical method rather than a physical method of cutting or polishing with abrasive grains, the damaged layer due to friction between the abrasive grains and the crystal surface is not generated.

The method of processing a surface of a nitride semiconductor crystal according to the present invention and the nitride semiconductor crystal obtained with the method will be described specifically with examples.

(Example 1)

Referring to Figs. 1 and 2, surface plate A 24 shown in Fig. 2 was used as surface plate 14 shown in Fig. 1, and a metal Na of 100 % purity was placed on surface plate A 24 fixed on rotation axis 13. Then a temperature was increased to 800 °C to form processing solution 15 as liquid Na. Surface plate A 24 was rotated at 50 rpm for 1 hour while a GaN crystal as nitride semiconductor crystal 11 mounted on crystal holder 12 was pressed against a surface thereof with processing solution 15 to process a surface of the GaN crystal. A depth of a surface scratch of the processed GaN crystal was measured with a contact type surface profiler. In addition, a thickness of a damaged layer of the processed GaN crystal was estimated with CL (cathode luminescence) of a cross section of the crystal. A maximum depth of a surface scratch of the processed GaN crystal was 0.05  $\mu\text{m}$  and an average thickness of a damaged layer was 1.5  $\mu\text{m}$ . The result is summarized in Table 2.

(Comparative Example 1)

A processing device similar to that in example 1 was used in a room temperature. While free abrasive grains each made of SiC and having a diameter of 10  $\mu\text{m}$  were supplied onto a surface of the surface plate and while the GaN crystal as the nitride semiconductor crystal mounted on the crystal holder was pressed against the surface of the surface plate supplied with the free abrasive grains, the surface plate was rotated at 50 rpm for 10 hours to process a surface of the GaN crystal. A maximum depth of a

surface scratch of the processed GaN crystal was 5  $\mu\text{m}$  and an average thickness of a damaged layer was 10  $\mu\text{m}$ . The result is summarized in Table 2.

(Comparative Example 2)

A surface of the GaN crystal was processed in a similar condition as in comparative example 1 except that free abrasive grains of 5  $\mu\text{m}$  were used. The result is summarized in Table 2.

(Example 2)

A surface of the GaN crystal was processed in a similar condition as in example 1 except that a processing time of the crystal surface was set to 5 hours. As a result, a maximum depth of a surface scratch was smaller than 0.01  $\mu\text{m}$ , that is, below sensitivity of measurement, and an average thickness of a damaged layer was smaller than 1  $\mu\text{m}$ , that is, below sensitivity of measurement. The result is summarized in Table 2.

(Example 3)

A surface of the GaN crystal was processed in a similar condition as in example 2 except that Na of 90 % purity was used as a processing solution. The result is summarized in Table 2. It is to be noted that, Fe, Mg, Ti, Sc, and V were detected as impurities included with Na as a result of measurement with glow discharge mass spectrometry.

(Examples 4-6)

A surface of the GaN crystal was processed using a processing solution as shown in Table 2 and with processing temperature and time as shown in Table 2. The result is summarized in Table 2.

(Examples 7-14)

A surface of the GaN crystal was processed using a processing solution as shown in Table 3 and with processing temperature and time as shown in Table 3. The result is summarized in Table 3.

(Example 15)

A surface of the GaN crystal was processed in a similar condition as in example

1 except that surface plate B 34 having grooves formed on a processing surface as shown in Fig. 3 was used as a surface plate. The groove of the surface plate B used in this example had depth D of 1 mm, width W of 1 mm and pitch P of 2 mm. The result is summarized in Table 4.

5 (Examples 16-18)

A surface of the GaN crystal was processed in a similar condition as in example 1 except that processing temperature and time were changed as shown in Fig. 4. The result is summarized in Table 4.

(Examples 19-22)

10 A surface of each kind of crystal was processed in a similar condition as in example 2 except that the crystal to be processed is replaced with a crystal as shown in Fig. 4. The result is summarized in Table 4.

Table 2

	Comparative Example 1	Comparative Example 2	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Nitride Semiconductor Crystal	GaN	GaN	GaN	GaN	GaN	GaN	GaN	GaN
Method of Processing	Abrasive Grain	Abrasive Grain	Surface Plate A					
Diameter of Abrasive Grain ( $\mu\text{m}$ )	10	5	-	-	-	-	-	-
Processing Solution	-	-	Na	Na	Na	Li	Ca	Li
Chemical Composition of Processing Solution (Mol%)	Na	-	100	100	90	-	-	-
Impurity	Li	-	-	-	-	100	-	100
Ca	-	-	-	-	-	-	100	-
Processing Condition	Temperature ( $^{\circ}\text{C}$ )	Room Temperature	800	800	800	950	800	
	Time (hr)	10	1	5	5	5	5	2
Maximum Depth of Surface Scratch ( $\mu\text{m}$ )	5	2	0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Average Thickness of Damaged Layer ( $\mu\text{m}$ )	10	8	1.5	< 1	< 1	< 1	< 1	< 1

\*Mg, Fe, V, Sc, and Ti as impurities

Table 3

	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
Nitride Semiconductor Crystal	GaN	GaN	GaN	GaN	GaN	GaN	GaN	GaN
Method of Processing	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A
Diameter of Abrasive Grains ( $\mu\text{m}$ )	-	-	-	-	-	-	-	-
Processing Solution	Na-Li	Na-Li	Na-Ca	Na-Ca	Na-Li	Na-Li	Na-Li	Li-Ca
Chemical Composition of Processing Solution (Mol%)	Na Li Ca Impurity	50 50 - -	50 50 - -	50 50 30 -	40 30 30 -	40 30 30 -	5 95 5 -	-
Processing Condition	Temperature ( $^{\circ}\text{C}$ )	800	800	800	800	800	800	800
Maximum Depth of Surface Scratch ( $\mu\text{m}$ )	Time (hr)	5	4	5	3	5	4	2
Average Thickness of Damaged Layer ( $\mu\text{m}$ )	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Table 4

	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22
Nitride Semiconductor Crystal	GaN	GaN	GaN	GaN	AlN	Al <sub>0.5</sub> Ga <sub>0.5</sub> N	InN	In <sub>0.5</sub> Ga <sub>0.5</sub> N
Method of Processing	Surface Plate B	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A	Surface Plate A
Diameter of Abrasive Grains (μm)	-	-	-	-	-	-	-	-
Processing Solution	Na	Na	Na	Na	Na	Na	Na	Na
Chemical Composition of Processing Solution (Mol%)	Na 100	Li -	Ca -	Impurity -	Temperature 800 °C	Time (hr) 1	Maximum Depth of Surface Scratch (μm) < 0.01	Average Thickness of Damaged Layer (μm) < 1
	100	-	-	-	800	20	< 0.01	< 1
					600	10	< 0.01	< 1
					1000	3	< 0.01	< 1
					800	5	< 0.01	< 1
					800	5	< 0.01	< 1

It is obvious from example 1 in comparison with comparative example 2 that, with Na used as one of the processing solutions of the present invention in place of the abrasive grains having a diameter of 5  $\mu\text{m}$ , the maximum depth of the surface scratch and the average thickness of the damaged layer were substantially decreased from 2  $\mu\text{m}$  to 0.05  $\mu\text{m}$  and from 8  $\mu\text{m}$  to 1.5  $\mu\text{m}$ , respectively. In addition, it is obvious from example 2 in comparison with example 1 that, by changing the processing time from 1 hour to 5 hours at a temperature of 800 °C, the maximum depth of the surface scratch less than 0.01  $\mu\text{m}$  and the average thickness of the damaged layer less than 1  $\mu\text{m}$  were attained and thus surface processing with an extremely high accuracy was enabled.

In addition, as shown in examples 4-8, highly accurate surface processing with the maximum depth of the surface scratch less than 0.01  $\mu\text{m}$  and the average thickness of the damaged layer less than 1  $\mu\text{m}$  is also possible using Li or Ca in place of or in combination with Na as the processing solution. In particular, as shown in examples 6, 8, 10, and 12-14, the processing speed is increased and the processing time can be decreased when the processing solution containing at least Li is used. In addition, as is obvious from example 9 in comparison with example 2, the processing time can be decreased from 5 hours to 1 hour when the surface plate having the grooves on the processing surface is used in place of the surface plate having a flat processing surface. In addition, as shown in examples 10-12, highly accurate surface processing with the maximum depth of the surface scratch less than 0.01  $\mu\text{m}$  and the average thickness of the damaged layer less than 1  $\mu\text{m}$  is enabled by setting the processing time to 20-3 hours as appropriate for the processing temperature of 300-1000 °C. Furthermore, as shown in examples 13-16, the crystal to be processed is not limited to the GaN crystal, and highly accurate surface processing of each kind of nitride semiconductor crystal such as an AlN crystal, an AlGaN crystal, an InN crystal, or an InGaN crystal is also possible.

It should be understood that the mode and examples disclosed herein are illustrative and non-restrictive in every respect. The scope of the present invention is defined by the terms of the claims, rather than the description above, and is intended to include any

modifications and changes within the scope and meaning equivalent to the terms of the claims.

#### Industrial Applicability

- 5 As described above, the present invention can be applied widely to a method of processing a surface of a nitride semiconductor crystal with a decreased depth of a surface scratch or a decreased thickness of a damaged layer, and a nitride semiconductor crystal obtained with the method.

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